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INJECTION OF HYDROGEN AND VACANCY-TYPE DEFECTS DURING DISSOLUTION OF ALUMINUM

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Formation of interfacial nanoscale voids in Al during room-temperature caustic corrosion was characterized by positron annihilation spectroscopy (PAS) and compared with measurements of deuterium absorption using secondary ion mass spectrometry (SIMS). The hypothesis was investigated that voids are created from vacancy-hydrogen (Vac-H) defects introduced during corrosion. Evidence for both mobile and immobile forms of absorbed hydrogen was obtained, the latter present within distances of 50 nm from the metal-oxide interface, where voids were also found. During corrosion, the immobile hydrogen was found only during discrete 1-2 min intervals of time separated by periods of 1-2 min when it was not present. Model calculations suggested that this transient behavior is consistent with repeated nucleation and dissolution of clusters of Vac-H defects. Only some aspects of the time-dependence of the void concentration from PAS corresponded with that of absorbed hydrogen; the former is believed to be influenced by metallic impurities.

INTRODUCTION

Recent positron annihilation spectroscopy (PAS) investigations have found evidence for nm-scale voids in aluminum, located in the metal within tens of nm from the metal/oxide interface (1-3). These interfacial voids result from either dissolution or oxide growth, suggesting that they form from vacancy-type defects injected by metal atom oxidation. PAS indicated that the internal surface of the voids was oxide-free and thus would be highly reactive if exposed at the surface during the course of passive corrosion. Thus, voids could function as pit initiation sites; in fact, correspondence between void number densities and rates of pit nucleation was demonstrated (4). However, questions remain about voids because the vacancy formation energy in Al apparently prohibits room-temperature vacancy injection. It should be noted that these metallic voids are distinct from oxide voids on Al detected recently by electron microscopy (5), although both void types originate from corrosion processes.

The interfacial metal voids may be related to vacancy-hydrogen defects in Al, evidence for which has recently appeared in the literature. Birnbaum and coworkers found large H concentrations in Al introduced by open-circuit caustic dissolution and
other room-temperature charging procedures, accompanied by either no change or a small contraction of the metal lattice parameter (6-8). They concluded that H was introduced as H-vacancy complex defects (Vac-H defects). These defects resulted in both H and vacancy concentrations exceeding equilibrium values at ambient temperature by several orders of magnitude. These large concentrations were possible because the H-vacancy binding energy in Al compensates for the vacancy formation energy. Bulk H bubbles resulting from H-vacancy coalescence were also detected following long periods of charging, some of which were on the same order of size as the interfacial voids detected by PAS (7). Fukai and coworkers have observed superabundant vacancies due to hydrogen-vacancy interactions in a number of metals, resulting from hydrogen absorption at high pressure, as well as from room-temperature electrodeposition processes (9,10). The formation of Vac-H defects in Al has been predicted in recent theoretical calculations (11).

In this paper, we investigate the relationship between interfacial voids in Al and hydrogen in the metal. Hydrogen and voids are introduced by simple open-circuit caustic dissolution, as in our previous work. Depth profiles of absorbed hydrogen near the metal surface were characterized using Secondary Ion Mass Spectrometry (SIMS) and compared with interfacial voids detected by PAS, in samples receiving identical treatments. Both spatial and temporal correlations between hydrogen and voids were examined. The results were interpreted with the aid of a mathematical model describing Vac-H defects formed by dissolution.

**EXPERIMENTAL**

The Al samples were 110 µm thick foils of 99.99 % purity (Toyo) and 99.9995 % purity (Alfa Aesar). The latter high-purity Al was used only for a set of PAS measurements; all SIMS experiments reported here used the 99.99 % Al foils. Dissolution of samples to be characterized with PAS was carried out at open circuit in aqueous 1 M NaOH solutions, at room temperature. For SIMS measurements, the solutions were 1 M NaOD in D₂O. Prior to dissolution experiments, the foils were electropolished in 20 % HClO₄ - ethanol solutions, at 5 °C and 30 V for 5 min. Electropolishing was necessary to obtain a flat reference surface allowing determination of the sputtering rate during SIMS, by measurement of the depth of sputtered crater. SIMS was carried out using a instrument at the Center for Microanalysis of Materials, University of Illinois (PHI Trift III ToF-SIMS). A 15 kV Ga⁺ beam was used for sputtering and a 2 kV Cs⁺ beam for analysis of negative secondary ions. The sputtered and analyzed areas were 400 x 400 µm, and 50 x 50 µm, respectively. During depth profiling, the sample was sputtered for typically 5 s and then analyzed for 8 s. Doppler broadening PAS measurements were carried out using the slow positron beam system at the University of Missouri-Kansas City (12). The spectrum of gamma radiation was measured at 2000 cps with a Ge solid state detector having an energy resolution of 1.5 keV at the annihilation photopeak energy of 511 keV. The positron source was 50 mCi ²²Na.
RESULTS AND DISCUSSION

Positron Annihilation Spectroscopy

Fig. 1 shows plots of the annihilation radiation lineshape parameter \( S \) vs. positron beam energy, for three representative 99.99 % Al foil samples. \( S \) has been normalized with respect to the bulk value, which represents a defect-free reference state. The beam energy controls the mean implantation depth of positrons, as indicated on the top scale. \( S \) is smaller than one in the surface oxide film. \( S \) values higher than one in the metal represent regions where a significant portion of annihilation events occurs at open-volume defects (e. g. vacancies, nm-scale voids). As indicated in Fig. 1, defect-containing regions were present in all samples, which extended to depths of order 100 nm, much larger than the oxide thickness of 2-5 nm. Plots of the lineshape parameters \( S \) and \( W \) (not shown) revealed that there was only one defect type in all samples, with \( S \) and \( W \) values of 1.05 and 0.9, respectively. The large \( S \) and low \( W \) of the defect indicated that it is a void of size greater than 1 nm, the surface of which was free of oxide. Since the dissolution rate in the NaOH solution was about 100 nm/min, these voids are in general not pre-existing but are formed by the dissolution process. These findings are the same as those of our previous measurements of as-received Al foils after NaOH dissolution (1,2).

The \( S \)-energy curves were simulated using the positron diffusion-annihilation equation to obtain quantitative information about the interfacial voids (13). The simulation
assumed a uniform void-containing layer adjacent along the oxide-metal interface, and yielded fit values of the characteristic S parameter \( S_d \) and thickness \( B_d \) of this layer. Details of the simulation procedure may be found elsewhere (1). Results are presented in Fig. 2 for 99.99 % Al and 99.9995 % Al foils. In the present samples, variations of \( S_d \) with dissolution time reflect changes of the void volume fraction in the defect layer (1). \( S_d \) reached a maximum at 1-4 min, and then decayed. This overall trend is the same as that reported previously for as-received foils. The initial increase of \( S_d \) of the high-purity foil was similar, but subsequently \( S_d \) decreased more slowly compared to the 99.99 % foil. Thus, the decay of \( S_d \) between the maximum and 18 min is due to impurities. Possibly, vacancies in the near-surface region can associate with impurities as low-S defects, instead of forming voids. Impurity effects will be treated in detail in a later report. The defect layer thickness (not shown) fluctuated around an average value of 63 nm.

![Graph showing the characteristic defect layer S parameter \( S_d \) vs. caustic dissolution time for 99.99 % Al and 99.9995 % Al foils. \( S_d \) is related to the volume fraction of voids in the metal adjoining the oxide-metal interface.](image)

**Secondary Ion Mass Spectrometry**

Fig. 3 shows the depth profiles of negative secondary ions for a typical 99.99 % Al sample, showing the major spectral peaks from the oxide film (AlO, O), the metal (Al, Al\(_2\)) and the deuterium-containing species (D, AlD). The time of 25 s corresponds to the decay of the AlO peak to half its maximum value, and to a sharp decrease of slope of the Al\(_2\) signal; both of these features mark the oxide-metal interface (14,15). D and AlD peaks were very low or absent in mass spectra of as-electropolished samples, but were
present in those of foils treated in NaOD. As illustrated in the Figure, the D signal was high in the oxide, reached a minimum at the interface, and then increased to an apparent plateau in the metal. Since the D profiles did not decay at large sputtering times, the penetration of D into the metal was evidently beyond the range of sputtered depths. The AlD signal was small in the oxide, rose to a maximum in the metal at the interface, and then decayed to low levels at sputter times greater than 300 s. Thus, AlD derived from a region in the metal close to the oxide-metal interface.

The D and AlD in the metal were normalized with respect to Al2, the largest signal in the bulk. This normalization permits comparison of AlD or D counts in samples treated for different times in NaOD. However, the D and AlD peaks cannot be compared to each other in terms of concentration, since their relative heights are in part determined by unknown sensitivity factors. Representative depth profiles of D and AlD in 99.99 %

![SIMS profiles after caustic dissolution of 99.99% Al for 14.5 min.](image)

Al are shown in Figs. 4 and 5, for the as-electropolished foil and dissolution times between 10 and 14.5 min. Sputtering time was converted to depth using the measured sputtering rate of 0.23 nm/s. The D profiles contain significant noise, and it is difficult to detect any trends with dissolution time. The maximum AlD signal, on the other hand, exhibited considerable but non-monotonic changes with dissolution time. According to Fig. 5, the AlD profile was flat at 10 min, increased sharply at 12 min, was low at 13 min and increased again at 14.5 min. AlD profiles, when detected, were confined within distances 50 nm from the metal-oxide interface. The appearance of such well-defined profiles indicates that the D associated with AlD is immobile at room temperature. In contrast, the estimated diffusivity of Vac-H defects, $4 \times 10^{-11}$ cm$^2$/s (7), implies that these defects should diffuse distances greater than 1 µm in the minimum time of 10 min between dissolution and SIMS measurements. Because of the apparently large penetration of the D profiles and their independence on treatment time, we assign the D peak to mobile Vac-H defects. The results of Birnbaum and coworkers suggest that this form predominates over interstitial hydrogen after room-temperature charging (6-8). The
Ald peak represents a "trapped" form of hydrogen distinct from the mobile Vac-H defects.

Figure 4. Representative D depth profiles after caustic dissolution of 99.99% Al. D counts are normalized with respect to Al\textsubscript{2} counts.

Figure 5. Representative Ald depth profiles after caustic dissolution of 99.99% Al. Ald counts are normalized with respect to Al\textsubscript{2} counts.

A large number of dissolution experiments were carried to follow the evolution of the Ald profiles in 99.99% Al foils. Fig. 6 shows the maximum Ald signals of these profiles. Remarkably, the Ald signal exhibited a series of "bursts" at intervals of 3-5 min;
during each burst, significant AlD was present and the profile resembled those at 10 and 12 min in Fig. 5. Individual bursts occupied 1-2 min, and were separated by periods of 1-2 min, during which the AlD depth profile was low and flat. The 50 nm range the AlD profiles compared favorably to the mean defect layer thicknesses of 63 nm obtained from PAS (Fig. 2). Thus, AlD was found in the interfacial region also occupied by voids; however, since its time dependence is much different from that of $S_d$, the AlD peak is not due to voids associated with hydrogen.

![Graph](https://example.com/graph.png)

Figure 6. Maxima of AlD and D profiles (e.g., Figs. 4-5) vs. caustic dissolution time.

An AlD-containing layer present at a given time during NaOD exposure would be subject to removal by metal dissolution. The lifetime of the layer can be estimated to be 0.5 min, from the Al dissolution rate of about 100 nm/min (2). This time agrees with the time of 0.5 - 1 min in Fig. 6, for the AlD level to decay after the maximum of each burst. Thus, we propose that AlD forms during the corrosion process, and that in every burst, the AlD "phase" appeared abruptly, was removed by dissolution, and then was produced again after 1-2 min passed. Sudden formation of AlD is suggestive of a nucleation process, which would be triggered by a critical supersaturation of a solute. Thus, we hypothesize that AlD was formed from mobile Vac-H (Vac-D) defects, which nucleated to create immobile clusters when a critical supersaturation of Vac-H defects was reached. Presumably, the bubbles (voids) detected by PAS are also due to Vac-H defects, but are distinct from these Vac-H clusters. The appearance of an AlD burst within the first minute may be due to unusually fast dissolution upon immersion, associated with a transient increase of the open-circuit potential observed during the first 4 min.

**Mathematical Model**
A mathematical model was developed to test whether the nucleation-dissolution hypothesis is consistent with the transient spikes of near-surface AlD detected by SIMS. The model is based on the transient diffusion equation for Vac-H defects. Knowledge of the Vac-H concentration derived from the model is also needed to predict conditions for void formation, but this was not attempted here. We assume that mobile Vac-H defects are injected at a given flux at the metal-oxide interface. Presumably, this flux is coupled to the rate of oxidation (dissolution) of surface Al atoms. The injection flux causes the concentration of Vac-H defects at the metal-oxide interface to increase with time, until the threshold value for cluster nucleation is reached. The balance on Vac-H defects written in the reference frame of the moving interface is

\[
\frac{\partial C_H}{\partial t} = V \frac{\partial C_H}{\partial x} + D_H \frac{\partial^2 C_H}{\partial x^2}
\]  

where \( C_H \) is the Vac-H concentration, \( V \) is the dissolution velocity, and \( D_H \) the Vac-H diffusivity. The subscript H is used because it is likely that all the mobile hydrogen in the metal is in the form of Vac-H defects (7). The origin of the x coordinate axis is on the interface, and the axis direction is toward the bulk Al.

The solution to Eq. 1 is subject to the boundary conditions that \( C_H = 0 \), both initially \((t = 0)\) and in the bulk Al \((x = \infty)\). The penetration depth of Vac-H defects can be estimated according to \( \delta_p \sim \sqrt{D_H \tau} \), where \( D_H \) is the defect diffusivity, and \( \tau \) a characteristic time of the dissolution experiments. Using \( D_H \sim 4 \times 10^{-11} \text{ cm}^2/\text{s} \) (8) and \( \tau \sim 100 \text{ s} \), we obtain \( \delta_p \sim 600 \text{ nm} \). Thus, the Vac-H defects diffuse to depths at least an order of magnitude larger than the AlD profile thickness indicated by Fig. 5. It is then appropriate to simplify the model by viewing the clusters to exist only in the plane of the interface itself. Thus, at the Al surface \((x = 0)\), the boundary condition is

\[
J_H = -VC_H|_{x=0} - D_H \frac{\partial C_H}{\partial x} \bigg|_{x=0} + 4\pi R_{cl}^2 \beta N_{cl}^0 k_m \left(C_H - C_{eq}^H\right)
\]

where \( J_H \) is the Vac-H injection rate per unit surface area, \( N_{cl}^0 \) is the number of as-nucleated clusters per unit surface area, \( C_{eq}^H \) is the Vac-H concentration in equilibrium with clusters, and \( k_m \) is a mass-transfer coefficient giving the rate of Vac-H diffusion to clusters. \( k_m \) should be approximately \( D_H / R_{cl} \), where \( R_{cl} \) is a characteristic radius of growing clusters. \( \beta \) is a numerical factor \((0 \leq \beta \leq 1)\) which accounts for cluster removal as the dissolving interface passes through the cluster layer; thus, the number of clusters at a given time is \( \beta(t)N_{cl}^0 \). \( \beta \) is nonzero only when clusters are present, when it is

\[
\beta = 1 - \frac{V(t - t_{nuc})}{\delta} \quad \text{for} \quad t_{nuc} \leq t \leq (t_{nuc} + \delta/V)
\]
where $t_{\text{nuc}}$ is the time of the most recent nucleation event, and $\delta$ is the thickness of the cluster-containing layer adjacent to the metal-film interface. Nucleation is initiated when $C_H$ at $x = 0$ reaches a critical supersaturation $\gamma C_{H}^{\text{eq}}$, where $\gamma > 1$. During the simulation, $t_{\text{nuc}}$ is continuously updated to the current time, if $C_H(x = 0)$ remains above $\gamma C_{H}^{\text{eq}}$. To account for rapid initial dissolution rates, the velocity $V$ was relaxed exponentially to a constant value during the first 4 min, and the injection rate $J_H$ was adjusted proportionally.

The model equations were cast in dimensionless form, which revealed that the normalized concentration at the interface, $\theta = \frac{C_H}{C_{H}^{\text{eq}}}$, is a function of several dimensionless parameters: time ($V^2 t/D_H$); distance ($Vx/D_H$); injection rate ($\phi = J_H/C_{H}^{\text{eq}} V$); nucleation site density ($\alpha = 4\pi R_{cl}^2 N_{cl}^{\text{eq}} V$); and cluster layer thickness ($V\delta/D_H$). No estimates were available for several parameters, e.g. $J_H$, $N_{cl}^{\text{eq}}$, and $\gamma$, and so direct calculations for the experimental conditions were not possible. Nonetheless, simulations were carried out which revealed trends relevant to the interpretation of the SIMS results. Figs. 7-8 show examples of results from model calculations. The range of dimensionless time in these plots corresponds to 17 min. Values of $\phi$ and $\gamma$ were chosen so the frequency of cluster nucleation events (Fig. 8) agreed with that of AlD bursts in Fig. 6.

![Figure 7](image-url)

**Figure 7.** Predicted concentrations of mobile Vac-H defects at $x = 0$, and Vac-H clusters, for a low value of $\alpha$ of 0.01. $\alpha$ is the dimensionless number density of nucleation sites.

The simulation results were sensitive to the choice of the nucleation site density $\alpha$; the model calculations in Figs. 7 and 8 represent extremes of this parameter. For small
\(\alpha\), clusters formed continuously (Fig. 7), but when \(\alpha\) was large, nucleation occurred as a series of bursts (Fig. 8). When \(\alpha\) was small, the consumption of Vac-H defects by growth of nucleated clusters was insignificant, and so the concentration of defects remained above the critical supersaturation for nucleation. On the other hand, for large \(\alpha\), cluster growth consumed Vac-H defects rapidly; thus, shortly after cluster nucleation, \(C_H(x=0)\) fell to a value near the equilibrium concentration, where it remained while clusters were present. Hence, nucleation was confined to a small time interval. When the clusters were eventually removed by dissolution, \(C_H(x=0)\) began to increase, triggering another nucleation event when it again reached the nucleation threshold, at which point the cycle repeated. Thus, when the nucleation site density was large, the predictions of cluster appearance followed by dissolution resembled the AID measurements in Fig. 6: a series of nearly evenly spaced time intervals when clusters/AID were present, separated by periods when none were found. These burst sequences were found for \(\alpha\) values as small as one. Therefore, the hypothesized cycles of nucleation and dissolution of Vac-H clusters are consistent with the AID bursts detected by SIMS.

![Figure 8. Predicted concentrations of mobile Vac-H defects at \(x = 0\), and Vac-H clusters, for a high value of \(\alpha\) of \(10^6\). \(\alpha\) is the dimensionless number density of nucleation sites.](image)

The results in Fig. 8 show that cyclic variations of the near-surface Vac-H concentration in the simulation accompanied cluster nucleation and dissolution. The amplitude of these cycles was adjustable through choices of \(\gamma\) and other model parameters. Thus, we cannot say whether the interfacial Vac-H concentration varied widely with time, or else was relatively constant. Since this concentration may provide the driving force for void (bubble) formation, the plot of \(S_d\) vs. time (Fig. 2) might be expected to show transient features coupled to the AID bursts, if the amplitude of \(C_H\) variations were significant. Fig. 2 shows some indication of such features: the initial rise of both \(S_d\) and AID coincide, and inflections of \(S_d\) occur just before the first two AID maxima at 20 s and 4 min. However, more PAS data are needed for this comparison to
be conclusive. Also, to fully describe the transient behavior of Vac-H defects, the likely association of these defects with metallic impurities should be probed experimentally and included in the model. As mentioned above, metal impurities are believed to explain the overall decrease of $S_d$ after 4 min, the magnitude of which decreases with increasing Al purity (2); impurity effects may be responsible for other transient features in the PAS data as well.

CONCLUSIONS

SIMS and PAS measurements were carried out to elucidate the relationship between hydrogen absorption and interfacial void formation in Al during open-circuit caustic dissolution. Both mobile and trapped forms of hydrogen were detected; the former was assigned to Vac-H defects and the latter tentatively to clusters of such defects. The trapped hydrogen was present during discrete intervals of dissolution time, separated by periods when it was not found. Model calculations indicated that these "bursts" were consistent with periodic nucleation and dissolution of Vac-H clusters, coupled to cyclic variations of the Vac-H concentration near the surface. The increase of the PAS parameter $S_d$ at the outset of dissolution paralleled that of the trapped hydrogen concentration, consistent with the hypothesized formation of both voids and clusters from mobile Vac-H defects. However, at later times the time-dependence of $S_d$ and immobile hydrogen concentration was different. Tentatively, we attribute this difference to an inhibition of void formation by metallic impurities, possibly due to preferential association between impurities and Vac-H defects. Thus, the results suggest that complex dynamic processes associated with absorbed hydrogen accompany this apparently simple corrosion process, involving mobile Vac-H defects, clusters of such defects, voids or $H_2$ bubbles, and possibly impurity-defect complexes. These processes have potentially important and unexplored implications for pitting corrosion, stress corrosion cracking, as well as general understanding of solute effects on corrosion.

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